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Sticking of He^4 on graphite and argon surfaces in presence of one phonon process

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Abstract : The sticking coefficient of He^4 gas particles on to the surfaces of graphite and argon is evaluated using the Greens function method. We explicitely look into the variation of sticking coefficient with the incident energy of gas particles from exact scattering T-Matrix of the system Contrary to the classical prediction we report a distribution of sticking coefficient with incident gas particle energy. This distribution is obtained for the sticking coefficients calculated in presence of bound state resonance and the phonon emission/absorption The exact time evaluation of the incident particles shows the expected nature and values of sticking coefficients of He^4 on graphite and argon surfaces.

Keywords : Sticking coefficient, T-Matrix, Greens function

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1. Introduction

The kinetics of adsorption and desorption of atoms physisorbed on solid surfaces have been reviewed experimentally and theoretically in recent few years [1–3]. Most of them tackled the problem by First Order Distorted Wave Born Approximation (FODWBA). In our previous work [4] we have shown that in the phonon assisted scattering of a gas-solid interaction the lower order DWBA may not be adequate to explain the total inelsatic component of the gas solid interaction.

On the other hand the mechanism behind the sticking in the quantum regime is understood from the observed sticking coefficient (SC) and the elastic scattering probabilities from the cold surfaces. A recent paper by Z W Gortel *et al* [5] shows that SC may lead to a value greater than one by FODWBA. They removed this difficulty by finding renormalised SC, specially for He-Ar and He-Graphite systems. Our aim is to find the SC by removing the overcounting of the scattering channels and to take into account all the inelastic components and the scattering channels. Because of low

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inelastic components and the scattering channels. Because of low energy incoming particles, the inelastic process becomes more important and responsible for sticking.

We therefore concentrate on phonon mediated physisorption of gas particles at normal incidence for low coverage at localised adsorption sites assuming that interaction between the adsorption sites is negligible.

We have proposed a Hamiltonian in terms of localised and phonon basis and changed the phonon basis into the localised basis by a canonical transformation. Hence we obtain the general theory for the temperature dependent bound state energy for the adsorbed system. The theory developed can then be used to calculate the sticking and inelastically scattered intensities for different bound states of the systems.

2. Theoretical model

The model Hamiltonian for the gas-solid system with localised and nonlocalised basis may be written as [6]

$$H = H_g + H_s + H_{\text{dyn}}, \tag{1}$$

where H_g is the Hamiltonian of the non interacting gas system in a box of length L. For just one shallow BS the three dimensional theory can be reduced to one dimensional theory and by introducing the second quantized creation/annihilation operators $C_k^\dagger / C_k$ in the state $|k>$ the first part of the Hamiltonian becomes

$$H_g = \sum \varepsilon_k C_k^\dagger C_k, \tag{2}$$

where $\varepsilon_k = \hbar^2 k^2 / 2m$ is the kinetic energy of free gas particle.

The second part of Hamiltonian (1) is that of the solid which in the harmonic approximation may be written as

$$H_s = \sum \hbar \omega_p b_p^\dagger b_p, \tag{3}$$

with $b_p^\dagger / b_p$, is the creation/annihilation operator of longitudinal acoustic phonons of frequency ω_p in the absence of gas.

The third term in equation (1) gives the gas-solid interaction. It consists of two parts, a static and a dynamic *i.e.* H_{gs}^{st} and H_{gs}^{dyn} respectively. Using the creation/annihilation operators the static part of the Hamiltonian becomes

$$H_{st} = \sum E_q C_q^\dagger C_q, \tag{4}$$

where E_q is the eigen value of the free particle state and BS energy E_n with $n = 0, 1, 2, 3, \ldots$

In fact the phonon-mediated gas solid interaction is accounted for by the dynamic part of the Hamiltonian which in the lowest order harmonic approximation is given by

$$H_{\text{dyn}} = \sum_{q,q-p} \chi_{q,q-p} C^{\dagger}_{q-p} \sum_{p} \omega_p^{-1/2} \left(b^{\dagger}_p + b_p\right) C_q, \tag{5}$$

where for local surface potential we have

$$\chi(q,q-p) = \left(\frac{\hbar}{2M_s N_s}\right)^{-1/2} \int \phi^{*}_{q-p}(x) \frac{dV_0(x)}{dx} \phi_q(x) dx. \tag{6}$$

Here $\phi_q(x)$'s are the eigen function of H_{st} denoted by the eigen value equation

$$\left[-\frac{\hbar}{2m}\frac{d^2}{dx^2} + V_0(x)\right]\phi_q(x) = E_q \phi_q(x). \tag{7}$$

Now with the help of the above equations, the Hamiltonian H in equation (1) takes the form,

$$H = \sum_{q} E_q C^{\dagger}_q C_q + \sum_{p} \hbar\omega_p b^{\dagger}_p b_p + \sum_{q,q-p} \chi(q-p,q) C^{\dagger}_{q-p} \sum_{p} \omega_p^{-1/2} (b^{\dagger}_p + b_{-p}) C_q. \tag{8}$$

with solid particle mass M_s and N_s the number of particles normalised in a box of length 'L'. Now by using the similarity transformation we reduce the above Hamiltonian to [6]

$$H = \sum_{q} E_q C^{\dagger}_q C_q + \sum_{p} \hbar\omega_p b^{\dagger}_p b_p + \sum_{q,q'} \chi(q-p,q)\chi(q'+p,q') \lambda_p^2 C^{\dagger}_{q'+p} C_{q'} C^{\dagger}_{q-p} C_q \left[\frac{\hbar\omega_p}{(E_q - E_{q-p})^2 - (\hbar\omega_p)^2}\right] \tag{9}$$

where $\lambda_p^2 = \dfrac{1}{\omega_p}$.

We have solved this Hamiltonian by T-Matrix formalism. We take the static surface potential as

$$V_0(x) = U_0(\exp^{-2\gamma(x-x_0)} - 2\exp^{-\gamma(x-x_0)}). \tag{10}$$

Now in order to obtain the Dyson equation for scattering T-Matrix, we write the single particle Green's function as

$$G_{km}(t) = \left\langle\left\langle \alpha_k(t), \alpha^{\dagger}_m(0)\right\rangle\right\rangle. \tag{11}$$

The Green's function may be written in the form of Dyson equation using above Hamiltonian and taking the fourier transformation as

$$G_{kk}(E) = G_k(0) + G_k(0) T G_{kn}(E), \tag{12}$$

which on iteration becomes

$$G_{kk}(E) = G_0(E) + G_0(E)TG_0(E), \tag{13}$$

where $$G_0(E) = \frac{1}{2\pi(E-E_k)}; T = \frac{2\pi\Delta_k}{1-\sum_q \frac{\Delta_q}{(E-E_q)}}$$

and $$\Delta_q = \sum_p |\chi(q,q-p)|^2 \lambda_p^2 n_{q-p}$$

$$\left(\frac{1}{E_q - E_{q-p} - \hbar\omega_p} - \frac{1}{E_q - E_{q-p} + \hbar\omega_p}\right). \tag{14}$$

Here 'q' is the momentum of the gas particle in the localised state and (q–p) is that in the BS. E is the effective final energy with transformed BS energy $E_{n'}$ is due to gas solid interaction and the continuum state energy.

The relative gas atom occupation number in the substrate maintained at substrate temperature T_s and at gas temperature T_g is

$$n_{q-p} = \exp\beta_s\left(|E_{n'}| - \beta_g|\mu|\right) \ll 1, \tag{15}$$

with, $\beta_s = \frac{1}{K_\beta T_s}; \beta_g = \frac{1}{K_\beta T_g}$ and μ the chemical potential of the gas which for He gas is taken here as 144°K [7].

Now while evaluating the $|\chi(q,q-p)|^2$ we consider the dimensionless parameters as [8]

$$\sigma_0^2 = \frac{2mU_0}{\hbar^2\gamma^2}; S^2 = \frac{2m|E_{n'}|}{\hbar^2\gamma^2}; r = \frac{2m\omega_d}{\hbar\gamma^2}; \xi = \gamma x; \xi_0 = \gamma_0 x_0$$

and the normalised BS wave function as $\phi_n(x) = \sqrt{\gamma} f_n(\xi)$ with

$$f_n(\xi) = (2\sigma_0)^{S_n}\Gamma^{(-1/2)}(2S_n)\binom{2S_n+n}{n}^{-1/2}$$

$$\exp(-\alpha_0 e^{-(\xi-\xi_0)}) e^{-S_n(\xi-\xi_0)} L_n^{2S_n}(2\sigma_0 e^{-(\xi-\xi_0)}), \tag{16}$$

where $S_n = \sigma_0 - n - \frac{1}{2}$; with $n = 0, 1, 2 \ldots$ and $L_n^{2S_n}(u)$ is a Laguerre Polynomial.

The continuum state wave functions of momentum 'q' normalised in a box of length 'L'; ($-L < x < L$), are given by $\phi_q(x) = (2L)^{-1/2} f(\eta;\xi); \eta = q/\gamma$ and

$$f(\eta;\xi) = \left|\frac{\Gamma(1/2-\sigma_0-i\eta)}{\Gamma(2i\eta)}\right| \exp\left(-\sigma_0 e^{-(\xi-\xi_0)} e^{-i\eta(\xi-\xi_0)}\right)$$

$$\Psi\left(1/2-\sigma_0+i\eta, 1+2i\eta, 2\sigma_0 e^{-(\xi-\xi_0)}\right), \tag{17}$$

where $\psi(a,b,z)$ is a confluent hypergeometric function that vanishes at $z \to \infty$. Again while evaluating the sums we have to invoke the thermodynamic limit *i.e.* $\sum_k \to (L/\pi)\int_0^\infty dk$ and perform the sums over phonon states for a Debye model *i.e.* $\sum_p \to (\frac{3N_s}{\omega_d^3})\int_0^{\omega_d} \omega_p^2 d\omega_p$. This leads to a real and a imaginary part of the T-Matrix.

The transition probability from the initial continuum to a final BS under the emission of phonon may be given by

$$R_{kn} = \frac{2\pi}{\hbar}\sum_{k-p}|ReT|^2 \exp\left\{-\frac{(E_{k-p}-E_k)}{K_\beta T_s}\right\}\delta(E_k - E_{k-p} - \hbar\omega_D). \quad (18)$$

Hence the transition probability from continuum gas state of the momentum k to all the BS is,

$$R_k = \sum_n R_{kn} \quad (19)$$

So the sticking coefficient for a particle of momentum k normalised by the flux of incoming particle τL defined by $\tau L = \frac{2Lm}{\hbar k}$ is

$$S_k = \frac{2mL}{\hbar k} R_k \quad (20)$$

Now we define the total sticking coefficient S as the average of S_k over the spectrum of thermal flux of incoming particles as [9]

$$S = \frac{\sum_k S_k j_k^{in}.(-n)n_k A}{\sum_k j_k^{in}.(-n)n_k A} = \left(\frac{\pi\hbar^2}{2mK_\beta T_g}\right)^{1/2}\sum_k kS_k n_k^{eq} \quad (21)$$

where the j_k^{in} is the incoming current density of particles of momentum $\hbar k$, and n is the normal to the solid surface of area A.

With $n_k^{eq} = \exp(\beta_q\mu - E_k\beta_s)$ we get the expression for sticking coefficient as

$$S = 16\left(\frac{\pi\hbar^2\gamma^2}{2mK_\beta T_g}\right)^{1/2} C^2\int_0^\infty dx\sqrt{x}[F(x)]^2$$

$$\left[\{G(r-S^2)\}^2 + \{\pi/2(r-S_n^2)\}^2\right]N_{xr}\exp(\beta_g\mu)\Theta(x-r) \quad (22)$$

with $$C = \int_0^\infty dy F(y)\frac{(y-S_n^2+S^2)}{S_n^2} \quad (23)$$

$$F(x) = \frac{\sinh(2\pi\sqrt{x})}{\sinh^2(\pi\sqrt{x})+\cosh^2(\pi\sigma_0)}\left|\Gamma(1/2+\sigma_0+i\sqrt{x}\right|^2$$

$$[x+(\sigma_0-n-1/2)^2]^2, \quad (24)$$

$$G(x) = r + \frac{x - s_n^2 + s^2}{2} \ln \left| \frac{r - (x - s_n^2 + s^2)}{r + (x - s_n^2 + s^2)} \right| \tag{25}$$

and

$$N_{xr} = \exp\left\{ \frac{\hbar^2 \gamma^2}{2mK_\beta T_s} (r - x) \right\} \tag{26}$$

3. Results and discussion

The essential feature of this work is based on the calculations of Sc of He^4 on cold graphite and solid argon surfaces with extended particle phonon interactions giving rise to the inelastic scattering in presence of resonant surface BS. Although the inelastic scattering is sufficiently weak in this case where only one or two phonons are created or destroyed, it is never negligible.

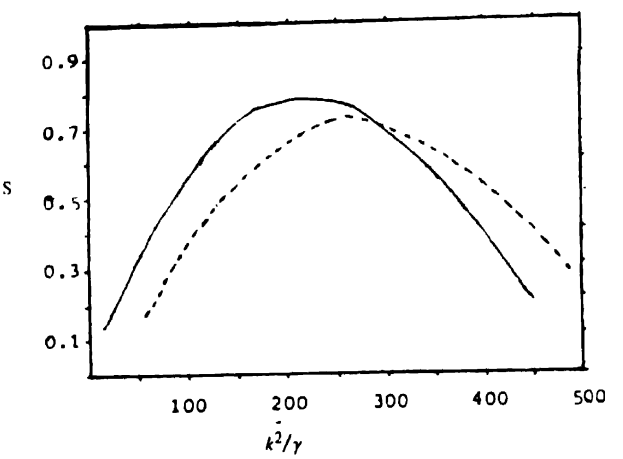

Figure 1. The variation of sticking coefficient with incident energy · (i) Dashed line for He–Ar and (ii) solid line for He-graphite system.

The variation of sticking coefficients for He-graphite and He–Ar systems with incident He gas particle energies has been shown in Figure 1. Clearly the sticking coefficients for both the cases show broad peaks at intermediate gas particle energies. This is in contrast with the classical prediction but is in good agreement with the experimental results confirming the fact that the experimental predictions for low energy particles need to be done quantum mechanically. The figure also indicates that for both the systems the sticking coefficients are less than unity. This suggests that the present T-matrix calculations of sticking co-efficients also takes care of the problem of overcounting of scattering events as was encountered in DWBA calculations. However at higher incident energies the nature of the sticking curve is that of the classical predictions confirming the fact that the particles at higher energies will be bounced back thereby reducing the sticking.

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